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PAN chelating membranes for simultaneous removal of metallic ions and organic pollutants from aqueous solution

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ABSTRACT

The chelating membrane was prepared by introducing amidoxime groups on to the surface of polyacrylonitrile (PAN) ultra filtration (UF) membrane to remove simultaneously the metallic ions and organic pollutants from aqueous solution. The performance of chelating membrane were investigated in terms of membrane flux, bovine serum albumin (BSA) rejection and removal rate of ions. The results showed that the amidoxime groups were successfully introduced onto PAN UF membrane, resulting in the rough membrane surface associated with increased hydrophobic properties. The chelating membrane exhibited a higher BSA rejection rate than original UF membrane, but had a relatively lower membrane flux. It was feasible to remove effectively Cu^{2+} and Pb^{2+} ions from aqueous solution by chelating membrane. Removal of metal ions for the chelating membrane followed this order: $Cu^{2+} > Pb^{2+} > Cd^{2+}$. As to the least preferentially adsorbed ion (Cd^{2+} ion), the removal rate could be significantly increased from 32% to73% in the presence of BSA due to the complexation of metal ion with protein.

Keywords: Chelating membrane; Surface modification; Metal ions; Adsorption; Amidoxime group

1. Introduction

In recent years, the scarcity of fresh water is raising concern worldwide with the industrial development and environmental pollution [1]. Industrial wastewater is a major source for spreading heavy metal ions (copper, lead, mercury and chromium) pollution in the accessible water sources, which poses a potential threat to human health. Therefore, it is of great significance to remove toxic heavy metal ions from the industrial waste water for obtaining clean water or non-threatening wastewater. There are a lot of methods to remove metal ions from aqueous solution including ion exchange, electrochemical operation, membrane separation and adsorption, etc [2,3]. Among these approaches, adsorption is one of the most widely adopted method [4]. Natural bio-sorbents are recommended because they are biodegradable, renewable, biocompatible, and nontoxic. As a byproduct in the furniture industry, the sawdust is a promising natural low-cost sorbent. Zhou et al. [5] prepared citric acid modified sawdust to remove divalent heavy metal ions (Cu^{2+}, Pb^{2+} and Cd^{2+}) from aqueous solutions. Zhang et al. [6] utilized the citric acid modified sawdust to simultaneously remove Cu^{2+} and methylene blue (MB) from the aqueous solutions. Furthermore, various polymer adsorbents are widely used to remove the metal ions from the wastewater. The adsorption capability is highly dependent upon the functional group son the adsorbent surfaces including carboxylate, hydroxyl, sulfate, phosphate, amide, amino [7] and amidoxime group, which can form a complexation with metal ions. Among them, amidoxime groups attract much attention due to the high tendency to form strong complexes with heavy metal ions.

Recently, the chelating membrane has been recognized as the most attractive and efficient method for

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removing metal ions from aqueous solution. The common feature of chelating membranes is containing a great deal of chelating group that can form strong complexes with metal ions. There is a vast number of literature about chelating membranes fabricated on the basis of different polymer materials, such as cellulose acetate (CA) [8–11], polyvinylidene fluoride (PVDF) [12,13], polyvinyl alcohol (PVA) [14–16], polysulfone (PSF) [17–20], polyacrylonitrile (PAN) [21–23] and so on. As to PAN chelating membrane, the previous literatures mainly focus on the application of PAN nano fiber membrane fabricated by the electro spinning technique [21–23]. However, the nano fiber membrane has a drawback of low productivity and high cost, which limits the wide application in aqueous waste treatment. It is essential to find a simple and easy way to prepare the chelating membrane. PAN ultrafiltration(UF) membrane is normally fabricated though a phase inversion method, which is widely adopted in industrial scale. UF membrane can remove effectively the organic contaminants from the polluted water [24], but it is in capable of removing the metal ions from the wastewater. The fabrication of chelating membranes through immobilizing functional groups into the UF membrane becomes an important option.

In the present study, the chelating membrane was prepared by introducing amidoxime group onto the PAN UF membrane surface. The chelating membrane were fully characterized by Fourier transform infrared spectrometer (FT-IR), energy dispersive spectrometer (EDS) and scanning electron microscope (SEM). The performance of chelating membrane was evaluated in terms of membrane flux,bovine serum albumin (BSA) rejection and removal rate of metal ions.

2. Experimental

2.1. Materials

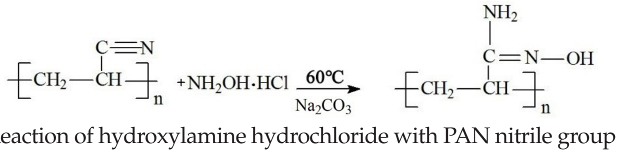
The PAN powders (M_w = 60,000 g/mol) and N, N-dimethylformamide (DMF) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. (China). Bovine serum albumin (BSA, M_w = 68,000 g/mol) were obtained from Solarbio (China). Hydroxylamine hydrochloride were obtained from Aladdin (China). Copper (II) chloride ($CuCl_2$, >99%) , lead (II) nitrate ($Pb(NO_3)_2$, >99%) and cadmium nitrate tetrahydrate ($CdN_2O_6{\cdot}4H_2O$ > 99%) were obtained from Tianjin Kemiou Chemical Reagent Co. Ltd. (China). All the chemicals were analytical grade.

2.2. Characterization

Fourier transform infrared (FT-IR) spectrometer from Perkin Elmer Inc. (USA) was employed to analyze the chemical structure. Scanning electron microscope (SEM) (JSM-7800F) from JEOL (Japan) was used to characterize the membrane morphology and structure. Atomic absorption spectroscopy (AAS) (Spectr 180–80) from Hitachi (Japan) was used to measure the concentration of metal ions in solution. Ultraviolet spectrophotometer (UV-1700PC) from Macy Instruments Inc. (China) was employed to analyze the BSA solution concentration.

2.3. Preparation of PAN chelating membrane

PAN powders were dried for 24 h at 60ºC before use, and then dissolved in DMF (casting solution: 17 wt%) under constant stirring at room temperature. Vacuum deaeration was conducted to eliminate the air bubble in casting solution before use. UF membranes were prepared by the L-S phase exchange method. The prepared UF membranes were soaked in the deionized water refreshing periodically.



Reaction of hydroxylamine hydrochloride with PAN nitrile group

The prepared PAN membrane was chemically modified with hydroxylamine hydrochloride to prepare the chelating membrane containing amidoxime groups. Hydroxylamine hydrochloride (3.47 g) and sodium carbonate (4.5 g) were added to a 1 L beaker with 500 ml deionized water where the PAN membrane was immersed in. The reaction was carried out at 60°C for 2 h. After reaction, chelating membranes were washed with deionized water for several times to remove the residual chemicals. The conversion of nitrile group on the surface of PAN UF membrane in to amidoxime group was calculated as follows [4]:

$$C_n = \frac{w_1 - w_0}{w_0}\frac{M_0}{M_1} \times 100\% \tag{1}$$

where C_n is conversion of nitrile group into amidoxime group, W_0 and W_1 is the weight of PAN membranes before and after chemical modification, respectively, $M_1$and M_0 is the molecular weight of hydroxylamine (33) and acrylonitrile monomer (53), respectively.

2.4. Membrane porosity measurement

After the water on membrane surface was drained out by filter paper, the membrane was weighed (W_w). The membrane was dried in a vacuum oven at 60°C for 4 h and then weighed (W_d).The porosity of membrane can be calculated as follows:

$$P_r = \frac{\dfrac{W_w - W_d}{\rho_{H_2O}}}{\dfrac{W_w - W_d}{\rho_{H_2O}} + \dfrac{w_d}{\rho_m}} \times 100\% \tag{2}$$

where P_r is porosity of membrane, W_w is the weight of wet membrane, W_d is the weight of dry membrane, ρ_{H2O} is the density of deionized water and is the density of PAN membrane.

2.5. Water flux measurement

The water flux of membrane was measured by UF cell from Shanghai SINAP Membrane Tech Co., Ltd (China). The membranes were pre-pressured at 0.15 MPa for 30 min to get stable structure, and then water flux of membrane was measured at 0.1 MPa. The water flux of membrane (at 25°C) can be calculated as follows:

$$J = \frac{V}{A \times T} \tag{3}$$

where J is the water flux of membrane, V is the volume of water through membrane, A is the effective area of membrane, T is the filtration time.

2.6. BSA rejection measurement

The BSA solution concentration was determined using a ultraviolet spectrophotometer. The BSA rejection of membrane (R) can be evaluated as follows:

$$\mathrm{R} = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \tag{4}$$

where C_F and C_P is the BSA concentrations of the feed and the permeate, respectively.

2.7. Static adsorption

The static adsorption of metal ions was carried out to evaluate the removal rate of ions and the adsorption capacity of chelating membrane. 200 mg chelating membrane (conversion degree: 2.5%) was immersed in a 200 ml aqueous ion solution (10 mg/L) with stirring at 25°C. The residual concentration of ions in solutions after adsorption time twas analyzed by a atomic absorption spectroscopy. The removal rate of ions was evaluated as follows:

$$\gamma = \frac{\left(C_0 - C_t\right)}{C_0} \times 100\% \tag{5}$$

where γ is the removal rate of ions, C_0 is the initial concentration of ion solution and C_t is the concentration of ions in solution after adsorption time t.

The adsorption capacity (Q) (mg/g) of chelating membrane can be calculated as follows:

$$Q = \frac{\left(C_0 - C_t\right)V}{m} \tag{6}$$

where V is the total volume of solution and m is the weight of dry chelating membrane.

2.8. Dynamic removal

The chelating membrane was fixed at the UF cell filled with 100 ml ion solution for dynamic removal of metal ions. UF experiment of ion solutions was performed and membrane flux was measured at 0.1 MPa. The ion concentration of the permeate was analyzed to evaluate the removal rate of ions.

3. Results and discussion

3.1. FTIR and EDS analyses

FTIR spectra was employed to identify the presence of certain functional groups on the chelating membrane surface because each specific chemical bond often showed a unique energy adsorption band. FTIR spectra of original PAN membrane and chelating membrane are presented in Fig. 1. Compared with PAN membrane, the chelating membrane showed different characteristic adsorption peaks. The strong and wide peak at about 3500~3000 cm^{-1} corresponded to O-H and N-H bonds [25]. The characteristic stretching vibration C-O and N-O absorption bands at 1687 cm^{-1} and 942 cm^{-1} were also observed [26]. It indicated that the amidoxime group was successfully introduced into the PAN membrane. In addition, both original membrane and chelating membrane exhibited the similar characteristic peak at about 2246 cm^{-1} corresponding to nitrile group (-CN) [27,28], suggesting that the nitrile group of PAN membrane was partially converted into amidoxime group.

The energy dispersive spectroscopy (EDS) was employed to determine the atomic percentage of various elements of membranes and results are shown in Table 1. After the chemical modification of PAN membrane, the atomic percentage of N and O elements in chelating membrane increased by 4.53 % and 10.6 %, respectively, while it decreased by 15.13 % for C element. The variation in atomic percentage of C, N and O elements could further testify the successful introduction of amidoxime group onto PAN membrane.

3.2. Membrane structure

SEM images of both original membrane and chelating membrane are presented in Fig. 2. It can be seen from Figs. 2a$_1$ and 2b$_1$ that the surface morphology of original membrane was much smoother than chelating membrane. The surface roughness of chelating membrane was mainly attributed to the introduction of amidoxime group onto

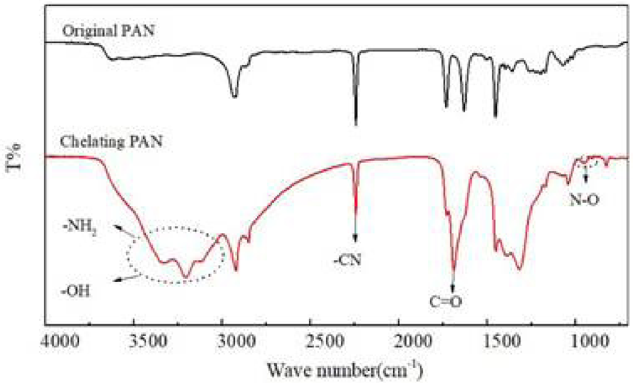


Fig. 1. FTIR spectra of PAN membrane and chelating membrane.

Table 1
Weight percent of elements based on EDS analysis

Element	Original membrane	Chelating membrane
C	68.59%	53.46%
N	24.41%	28.94%
O	7%	17.60%

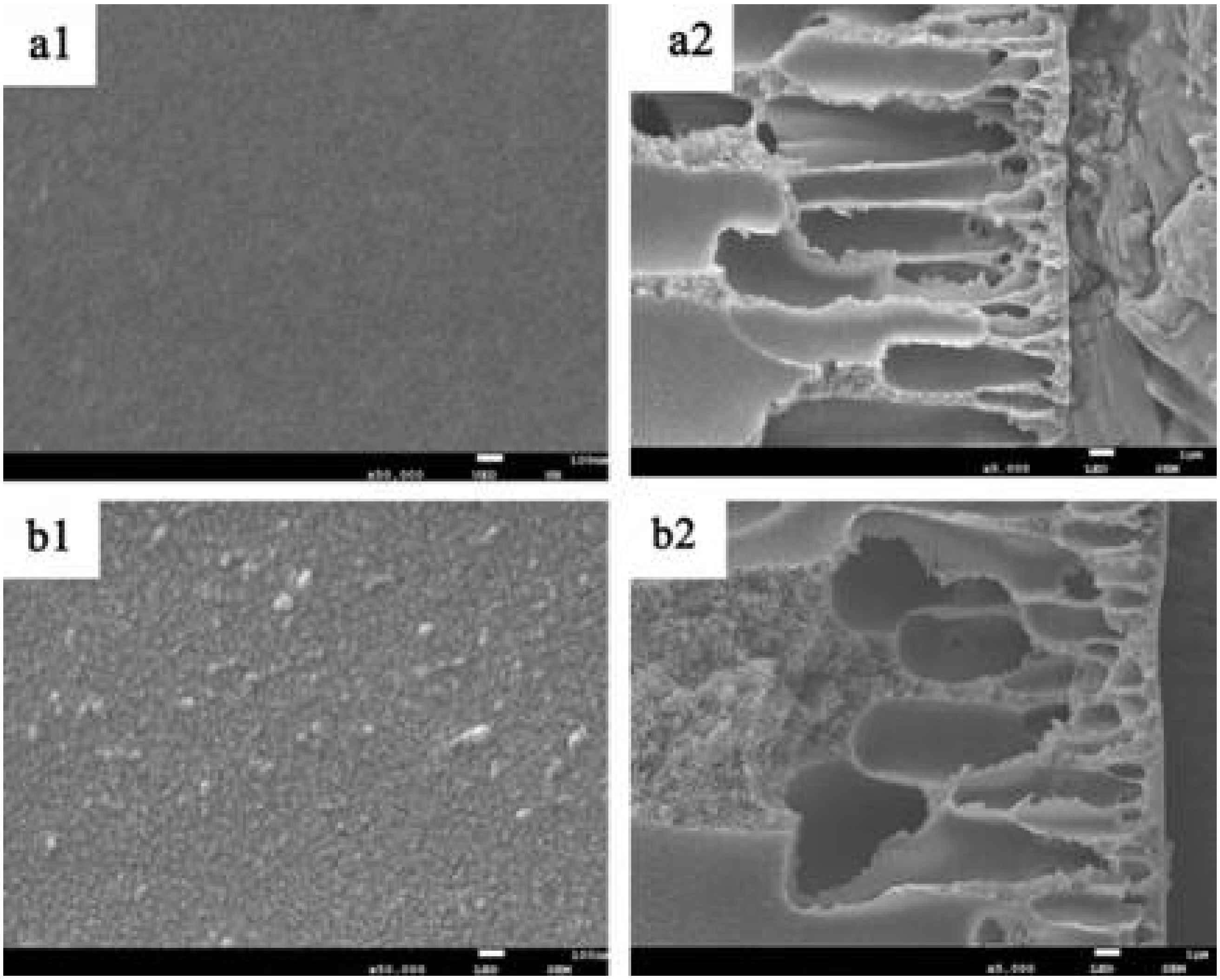


Fig. 2. Surface structure of original membrane (a_1) and chelating membrane (b_1), cross-sectional structure of original membrane (a_2) and chelating membrane (b_2).

the surface of PAN membrane, leading to the occlusion of membrane pores. As a result, the porosity of chelating membrane (80.67%) was slightly less than that of original PAN membrane (83.08%). The cross-sectional structure of membranes was illustrated in Figs. $2a_2$ and $2b_2$. Both original membrane and chelating membrane exhibited similar finger-like pore structure. No obvious evidence showed the presence of amidoxime groups on the pore wall of chelating membrane. It indicated the surface modification had a little influence on the cross-sectional structure of chelating membrane.

3.3. Filtration performance of BSA solution

The BSA rejection is an important index reflecting the filtration performance of UF membrane. The rejection rate of BSA solution for both original membrane and chelating membrane were examined to investigate the influence of surface modification on the UF membrane performance.

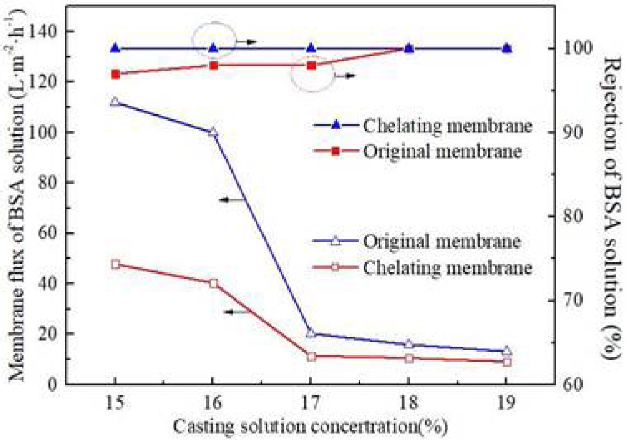


Fig. 3. Variations of BSA rejection and filtration flux for original membrane and chelating membrane with the casting solution concentration (BSA solution concentration: 200 mg/L).

Fig. 3 shows that chelating membrane possessed a higher BSA rejection rate (100%) than original membrane (above 98%) in the range of casting solution concentration. It indicated that the introduction of amidoxime groups on the PAN membrane surface during the chemical modification could improve the BSA rejection performance. As mentioned before, the chemical modification changed the surface morphology of membrane, resulting in the blockage of pore, thereby reducing the porosity of membrane. The low porosity of chelating membrane was beneficial for the enhancement of BSA rejection performance. As far as BSA rejection was concerned, it could conclude that the chemical modification had a positive influence on the UF membrane performance.

In order to further investigate the influence of chemical modification on the filtration performance of UF membrane, the membrane flux of BSA solution was measured, and the results are shown in Fig. 3. Obviously,the chelating membrane exhibited a lower filtration flux of BSA solution than original membrane. It was mainly due to the fact that the introduction of amidoxime groups changed the surface roughness of chelating membrane, thereby enhancing the hydrophobicity of membrane, which was validated by variations of contact angle of membranes. The contact angle of chelating membrane (46.11°) was much higher than that of original PAN membrane (36.62°), indicating the surface modification augmented the hydrophobic properties of chelating membranes. As far as membrane flux was concerned, it concluded that the chemical modification had a negative influence on the UF membrane performance.

3.4. Static removal behaviors

In order to investigate the feasibility of chelating membrane for removing the metal ions, the static adsorption of metal ions was conducted. Fig. 4 shows the time-dependent adsorption behaviors of chelating membrane in removing lead, cadmium and copper ions from aqueous solution. It could be seen that the removal rate of Cu^{2+}, Pb^{2+} and Cd^{2+} ions increased rapidly in the first 1 h and then augmented slowly and approached the adsorption equilibrium in about 7 h. The removal rate of ions dramatically increased during the initial period due to the fact that there were a lot of amidoxime groups on the surface of chelating membrane. The static adsorption of metal ions depended highly upon the number of available functional groups (amidoxime group) on the surface of chelating membrane.

The effect of solution pH values on the adsorption capacity of chelating membrane for different metal ions is presented in Fig. 5. The adsorption experiments were performed in a pH range of 2–7 in order to avoid the precipitation of metal ions under alkaline conditions. As expected, the adsorption capacity of chelating membrane for metal ions showed an increasing tendency with pH value, which was consistent with the previous study [29]. It could be attributed to the fact that low H^+concentration may compete with the metal ion for the coordination with active amidoxime group and subsequently lower the adsorption capacity at low pH values. Differently, the adsorption capacity of chelating membrane exhibited a significant increase at high pH value for Cu^{2+} and Pb^{2+} ions, while a moderate increase for Cd^{2+} ion. It was mainly due to the strong interaction betweenCu^{2+} and Pb^{2+}ions and amidoxime group.

Fig. 6 shows the effect of the conversion degree of chelating membrane on the adsorption capacity for different ions. The conversion degree of nitrile group into amidoxime group varied with the reaction condition such as hydroxylamine hydrochloride concentration or reaction time. In this study, the conversion degree of chelating membrane was controlled within a relatively lower level (< 30%), because the chelating membrane with a high conversion degree was very brittle and easily broken. It can be seen from Fig. 6 that the adsorption capacity for Cu^{2+} and Pb^{2+} ions increased with the increment of the conversion degree of chelating membrane due to the strong interac-

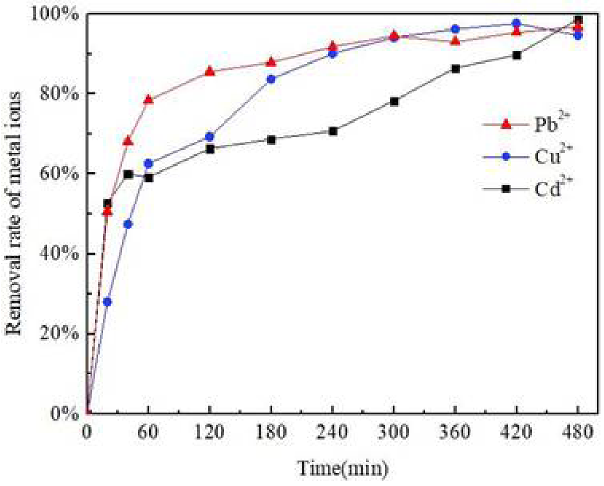


Fig. 4. Variation of removal rate for different ions versus time. (ion concentration: 10 mg/L; solution volume: 200 ml; chelating membrane: 200 mg; conversion degree: 2.5%).

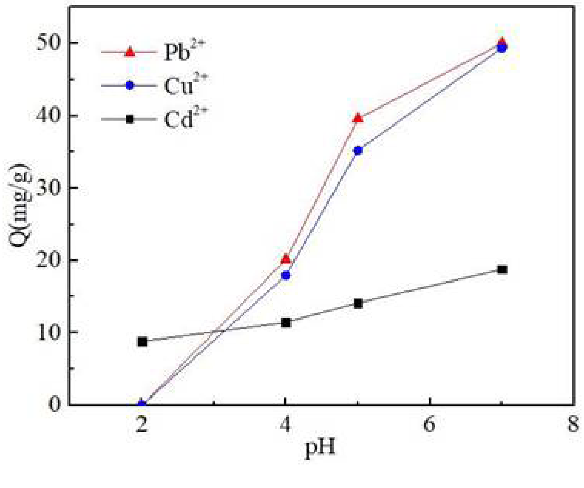


Fig. 5. Effect of pH value on the adsorption capacity for different ions (ion concentration: 10 mg/L; solution volume: 200 ml; chelating membrane: 200 mg; conversion degree: 2.5%; adsorption time: 1 h).

tion between Cu^{2+} and Pb^{2+} ions and amidoxime group. However, the conversion degree of chelating membrane had a negligible influence on the adsorption capacity for Cd^{2+} ion owing to the weak complexation between amidoxime group and Cd^{2+} ion.

3.5. Competitive removal of different ions

The competitive removal of Cu^{2+}, Pb^{2+} and Cd^{2+} ions from aqueous solution was conducted under the condition that the concentration of each kind of ion was same (3.33 mg/L). The total ion concentration in solution was approximately about 10 mg/L. Fig. 7 shows that the chelating membrane had a significantly higher removal rate for Cu^{2+} ion than for Pb^{2+} and Cd^{2+} ion. After 6 h, the removal rate of Cu^{2+} ion was 100%. The removal rate of Pb^{2+} ion achieved the equilibrium value after 3 h, about 19%. However, the removal rate of Cd^{2+} ion was almost 0. It confirmed that the chelating membrane removed Cu^{2+} ion the most preferentially, followed by Pb^{2+} ion, Cd^{2+} ion the least preferentially, due to the most strong interaction between Cu^{2+}ion and amidoxime group. The preferential removal of Cu^{2+} ion might be attributed to the minimum of ionic radius (0.073 nm) among these ions.

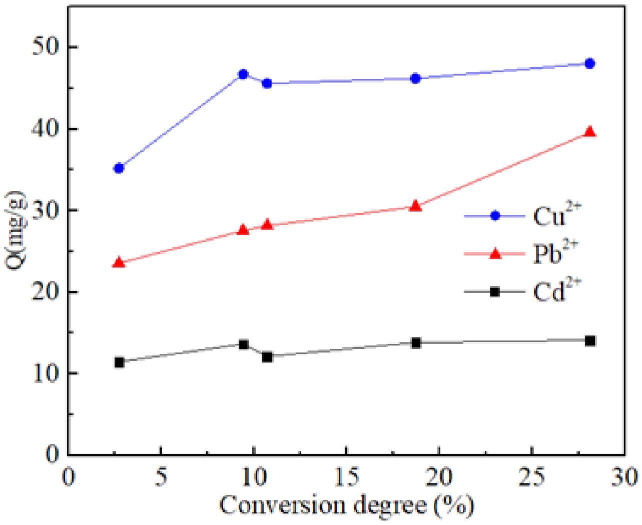


Fig. 6. Effect of the conversion degree of chelating membrane on the adsorption capacity for different ions. (ion concentration: 10 mg/L; solution volume: 200 ml; chelating membrane: 200 mg; adsorption time: 1 h).

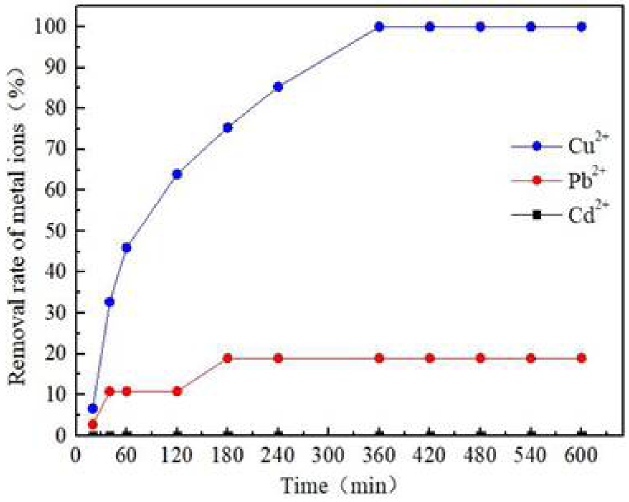


Fig. 7. Competitive adsorption of different metal ions for chelating membrane (Cu^{2+} ion concentration: 3.33 mg/L; Pb^{2+} ion concentration: 3.33 mg/L; Cd^{2+} ion concentration: 3.33 mg/L; solution volume: 200 ml; chelating membrane: 200 mg; conversion degree: 2.5%.).

3.6. Dynamic removal behaviors

The purpose of this study is to remove the metallic ion from the industrial wastewater by the chelating membrane. UF experiment of ion solution was conducted using the UF cell to evaluate the dynamic removal of metal ions for chelating membrane (conversion degree: 2.5%). The solution volume was 100 ml. The concentration of each kind of ion was 1.67 mg/L. Table 2 shows that chelating membrane could remove completely both Cu^{2+} and Pb^{2+} ions from the aqueous solution. However, the removal rate of Cd^{2+} ion was still very low (32%), due to the weak interaction between Cd^{2+} ion and amidoxime groups. Obviously, it was feasible to remove effectively Cu^{2+} and Pb^{2+} ions from the industrial wastewater by chelating membrane at a relatively low ion concentration.

In fact, the metallic ions and organic pollutants may coexist in the industrial wastewater. It is necessary to investigate whether the chelating membrane can remove simultaneously metal ions and organic contaminants from the industrial wastewater. The function of traditional UF membrane is the rejection of the macromolecular organic contaminants. The introduction of functional groups onto UF membrane endows the chelating membrane can remove effectively the metallic ions from aqueous solution. Theoretically, the chelating membrane can remove effectively metal ions and organic contaminants at the same time. UF experiment of ion solutions mixing with BSA solution (C = 200 mg/L) was conducted under the same operation condition. As illustrated in Table 3, the chelating membrane could remove completely Cu^{2+}, Pb^{2+} ions and BSA from aqueous solution. Surprisingly, the removal rate of Cd^{2+} ion significantly increased to 73% in the presence of BSA. It indicated the presence of BSA could augment the removal rate of certain metal ion that was the least preferentially removed by the chelating membrane. The improvement of Cd^{2+} ion removal rate was might due to the complexation of metal ion with BSA protein.

Table 2
Dynamic removal of metal ions(no BSA)

Metal ions	Removal rate	Membrane flux ($L \cdot m^{-2} \cdot h^{-1}$)
Cu^{2+}	100%	83.57
Pb^{2+}	100%	
Cd^{2+}	32%	

Table 3
Dynamic removal of metal ions (mixed with BSA solution)

Metal ions	Removal rate	BSA Rejection	Membrane flux ($L\cdot m^{-2}\cdot h^{-1}$)
Cu^{2+}	100%	100%	
Pb^{2+}	100%	100%	35.19
Cd^{2+}	73%	100%	

4. Conclusions

In this study, the chelating membrane was successfully fabricated through chemical modification of PANUF membrane. The surface morphologies of chelating membrane became much more rough owing to introduction of amidoxime groups, thereby increasing the hydrophobic properties. The chelating membrane exhibited a higher BSA rejection rate than original UF membrane. However, the chelating membrane had a relatively lower filtration flux of BSA solution due to the increased hydrophobicity of membrane. It was feasible to remove effectively Cu^{2+} and Pb^{2+} ions from aqueous solution by chelating membrane containing amidoxime groups. The chelating membrane had a significantly higher removal rate for Cu^{2+} ion than for Pb^{2+} and Cd^{2+} ion, suggesting that Cu^{2+} ion was the most preferentially removed, owing to the strong interaction between Cu^{2+}ion and amidoxime group. As to the least preferentially removed metal ion, the removal rate of Cd^{2+} ion could be significantly increased from 32% to 73% in the presence of BSA,due to the complexation of metal ion with protein. Meanwhile, the chelating membrane could completely rejected BSA from aqueous solution. The chelating membrane can be recognized as a highly efficient and promising method for the simultaneous removal of metallicions and organic contaminants from the industrial wastewater.

References

[1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature, 452 (2008) 301–310.

[2] R.K. Nagarale, G.S. Gohil, V.K. Shahi, Recent developments on ion-exchange membranes and electro-membrane processes, Adv. Colloid Interface Sci., 119 (2006) 97–130.

[3] X. Wang, Nano materials as sorbents to remove heavy metal ions in wastewater treatment, J. Environ. Anal. Toxicol., 2 (2012) 154–160.

[4] B. Podkościelna, D. Kołodyńska, Z. Hubicki, B. Gawdzik, A. Bartnicki, Synthesis, characterization and application of a new methylenethiol resins for heavy metal ions removal, Sep. Sci. Technol., 51 (2016) 2501–2510.

[5] X. Gu, Adsorption of divalent heavy metal ions from aqueous solution by citric acid modified pine sawdust, Sep. Sci. Technol., 50 (2015) 245–252.

[6] R. Zhang, Y. Zhou, X. Gu, J. Lu, Competitive adsorption of methylene blue and Cu^{2+} onto citric acid modified pine sawdust, Clean-Soil Air Water, 43 (2015) 96–103.

[7] F. Huang, Y. Xu, S. Liao, D. Yang, Y.L. Hsieh, Q. Wei, Preparation of amidoxime polyacrylonitrile chelating nano fibers and their application for adsorption of metal ions, Materials, 6 (2013) 969–980.

[8] G. Arthanareeswaran, P. Thanikaivelan, N. Jaya, D. Mohan, M. Raajenthiren, Removal of chromium from aqueous sulfonated poly (ether ether ketone) solution using cellulose acetate and blend ultra filtration membranes, J. Hazard. Mater., 139 (2007) 44–49.

[9] Z. Chen, M. Deng, Y. Chen, G. He, Preparation and performance of cellulose acetate/polyethyleneimine blend micro filtration membranes and their applications, J. Membr. Sci., 235 (2004) 73–86.

[10] A. Nagendran, A. Vijayalakshmi, D.L. Arockiasamy, K.H. Shobana, D. Mohan, Toxic metal ion separation by cellulose acetate/sulfonated poly(ether imide) blend membranes: effect of polymer composition and additive, J. Hazard. Mater., 155 (2008) 477–485.

[11] G.S. Chauhan, S.C. Jaswal, M. Verma, Post functionalization of carboxy methylated starch and acrylonitrile based networks through amidoximation for use as ion sorbents, Carbohyd. Polym., 66 (2006) 435–443.

[12] E. Salehi, S.S. Madaeni, F. Heidary, Dynamic adsorption of Ni (II) and Cd (II) ions from water using 8-hydroxyquinoline ligand immobilized PVDF membrane: Isotherms, thermodynamics and kinetics, Sep. Purif. Technol., 94 (2012) 1–8.

[13] L. Song, X. Zhao, J. Fu, X. Wang, Y. Sheng, X. Liu, DFT investigation of Ni (II) adsorption onto MA-DTPA/PVDF chelating membrane in the presence of coexistent cations and organic acids, J. Hazard. Mater., 199–200 (2011) 433–439.

[14] H. Bessbousse, T. Rhlalou, J.F. Verchère, L. Lebrun, Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing Poly (ethyleneimine) in a Poly (vinyl alcohol) matrix, J. Membr. Sci., 307 (2008) 249–259.

[15] H. Bessbousse, J.F. Verchère, L. Lebrun, Characterisation of metal-complexing membranes prepared by the semi-interpenetrating polymer networks technique. Application to the removal of heavy metal ions from aqueous solutions, Chem. Eng. J., 187 (2012) 16–28.

[16] L. Lebrun, F. Vallée, B. Alexandre, Q.T. Nguyen, Preparation of chelating membranes to remove metal cations from aqueous solutions, Desalination, 207 (2007) 9–23.

[17] H.A. Tsai, H.C. Chen, K.R. Lee, J.Y. Lai, Study of the separation properties of chitosan/polysulfone composite hollow-fiber membranes, Desalination, 193 (2006) 129–136.

[18] R. Kumar, A.M. Isloor, A.F. Ismail, Preparation and evaluation of heavy metal rejection properties of polysulfone/chitosan, polysulfone/N-succinyl chitosan and polysulfone/N -propylphosphonyl chitosan blend ultra filtration membranes, Desalination, 350 (2014) 102–108.

[19] K.N. Han, B.Y. Yu, S.Y. Kwak, Hyper branched poly (amidoamine)/polysulfone composite membranes for Cd (II) removal from water, J. Membr. Sci., 396 (2012) 83–91.

[20] G. Pei, G. Cheng, Q. Du, Preparation of chelating resin filled composite membranes and selective adsorption of Cu (II), J. Membr. Sci., 196 (2002) 85–93.

[21] P.K. Neghlani, M. Rafizadeh, F.A. Taromi, Preparation of aminated-polyacrylonitrile nano fiber membranes for the adsorption of metal ions: comparison with microfibers, J. Hazard. Mater., 186 (2011) 182–189.

[22] K. Saeed, S. Haider, T.J. Oh, S.Y. Park, Preparation of amidoxime-modified polyacrylonitrile (PAN-oxime) nano fibers and their applications to metal ions adsorption, J. Membr. Sci., 322 (2008) 400–405.

[23] N. Horzum, T. Shahwan, O. Parlak, M.M. Demir, Synthesis of amidoximated polyacrylonitrile fibers and its application for sorption of aqueous uranyl ions under continuous flow, Chem. Eng. J., 213 (2012) 41–49.

[24] J. Decarolis, S. Hong, J. Taylor, Fouling behavior of a pilot scale inside-out hollow fiber UF membrane during dead-end filtration of tertiary wastewater, J. Membr. Sci., 191 (2001) 165–178.

[25] F. Burel, H. Oulyadi, C. Bunel, V. Grishchenko, N. Busko, A. Barantsova, V. Boiko, Synthesis and structural characterization of a liquid polyisoprene bearing amidoxime end groups, J. Polym. Res., 18 (2011) 2265–2273.

[26] F.T. Chi, H.U. Sheng, J. Xiong, X.L. Wang, Adsorption behavior of uranium on polyvinyl alcohol-g-amidoxime: physico chemical properties, kinetic and thermodynamic aspects, Sci. China Chem., 56 (2013) 1495–1503.

[27] G. Zong, H. Chen, R. Qu, C. Wang, N. Ji, Synthesis of polyacrylonitrile-grafted cross-linked N-chlorosulfonamidated polystyrene via surface-initiated ARGET ATRP, and use of the resin in mercury removal after modification, J. Hazard. Mater., 186 (2011) 614–621.

[28] Y. Wang, Z. Gu, J. Yang, J. Liao, Y. Yang, N. Liu, J. Tang, Amidoxime-grafted multiwalled carbon nanotubes by plasma techniques for efficient removal of uranium(VI), Appl. Surf. Sci., 320 (2014) 10–20.

[29] S. Deng, J.P. Chen, Aminated polyacrylonitrile fibers for lead and copper removal, Langmuir, 19 (2003) 5058–5064.